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U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE

ATTORNEY'S DOCKET NO.

H 3475 PCT/US

U.S. APPLICATION NO. 09/7808961

TRANSMITTAL LETTER TO THE UNITED STATES
DESIGNATED/ELECTED OFFICE (DO/EO/US)
CONCERNING A FILING UNDER 35 U.S.C. 371INTERNATIONAL APPLICATION NO.
PCT/EP99/07143INTERNATIONAL FILING DATE
September 25, 1999PRIORITY DATE CLAIMED
October 6, 1998

TITLE OF INVENTION

IMPACT-RESISTANT EPOXIDE RESIN COMPOSITIONS

APPLICANT(S) FOR DO/EO/US

Hubert Schenkel

Applicant herewith submits to the United States Designated/Elected Office (EO/DO/US) the following items and other information:

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
 2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
 3. ☐ This express request to begin national examination procedures (35 U.S.C. 371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39 (1).
 4. ☒ A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.
 5. ☒ A copy of the International Application as filed (35 U.S.C. 371(c)(2)).
 - a. ☐ is transmitted herewith (required only if not transmitted by the International Bureau).
 - b. ☒ has been transmitted by the International Bureau.
 - c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).
 6. ☒ A translation of the International Application into English (35 U.S.C. 371(c)(2)).
 7. ☒ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3))
 - a. ☐ are transmitted herewith (required only if not transmitted by the International Bureau).
 - b. ☐ have been transmitted by the International Bureau.
 - c. ☐ have not been made, however, the time limit for making such amendments has NOT expired.
 - d. ☒ have not been made and will not be made.
 8. ☐ A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
 9. ☒ An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)). UNEXECUTED
 10. ☐ A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).
- Items 11. to 16. below concern other document(s) or information included:
11. ☐ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
 12. ☐ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
 13. ☒ A **FIRST** preliminary amendment
 - ☐ A **SECOND** or **SUBSEQUENT** preliminary amendment.
 14. ☐ A substitute specification.
 15. ☐ A change of power of attorney and/or address letter.
 16. ☐ Other items or information:

"Express Mail" mailing label number EL615776154US

U.S. Application No. (If known, see 37 CFR 1.5) 09/806961		INTERNATIONAL APPLICATION NO. PCT/EP99/07143		ATTORNEY'S DOCKET NUMBER H 3475 PCT/US	
17. The following fees are submitted: BASIC NATIONAL FEE (37 CFR 1.492(a)(1)-(5)): Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO and International Search Report not prepared by the EPO or JPO..... \$1000.00 International preliminary examination fee (37 CFR 1.482) not paid to USPTO but International Search Report prepared by the EPO or JPO..... \$860.00 International preliminary examination fee (37 CFR 1.482) not paid to USPTO but international search fee (37 CFR 1.445(a)(2)) paid to USPTO \$710.00 International preliminary examination fee paid to USPTO (37 CFR 1.482) but all claims did not satisfy provisions of PCT Article 33(1)-(4) \$690.00 International preliminary examination fee paid to USPTO (37 CFR 1.482) and all claims satisfied provisions of PCT Article 33(1)-(4)..... \$100.00				CALCULATIONS PTO USE ONLY	
ENTER APPROPRIATE BASIC FEE AMOUNT =				\$	860
Surcharge of \$130.00 for furnishing the oath or declaration later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date 37 (CFR 1.492(e)).				\$	0
CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE		
Total Claims	29 - 20 =	9	9 X \$18.00	\$	162
Independent Claims	3 - 3 =	0	0 X \$80.00	\$	0
Multiple dependent claims (s)(if applicable)			0 + \$270.00	\$	0
TOTAL OF ABOVE CALCULATIONS				=	\$ 1022
Reduction of 1/2 for filing by small entity, if applicable. A Small Entity Statement must also be filed. (Note 37 CFR 1.9, 1.27, 1.28).				\$	0
SUBTOTAL				=	\$ 1022
Processing fee of \$130.00 for furnishing the English translation later the <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492(f)).				\$	0
TOTAL NATIONAL FEE				=	\$ 1022
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). \$40.00 per property				\$	0
TOTAL FEES ENCLOSED				=	\$ 1022
Amount to be:				\$-----	
refunded:					
charged:				\$	1022.00
a. <input type="checkbox"/> A check in the amount of \$_____ to cover the above fees is enclosed. b. <input checked="" type="checkbox"/> Please charge my Deposit Account No. <u>01-1250</u> in the amount of \$ <u>1022.00</u> to cover the above fees. A triplicate copy of this sheet is enclosed. Order No. <u>01-0293</u> . c. <input checked="" type="checkbox"/> The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. <u>01-1250</u> . A duplicate copy of this sheet is enclosed. NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137 (a) or (b)) must be filed and granted to restore the application to pending status.					
SEND ALL CORRESPONDENCE TO:		Henkel Corporation, Law Dept. 2500 Renaissance Blvd., Suite 200 Gulph Mills, PA 19406		SIGNATURE: <u>Kimberly R. Hild</u> Kimberly R. Hild NAME ATTORNEY FOR APPLICANT 39,224 REGISTRATION NUMBER	

09/806961

JC08 Rec'd PCT/PTO 06 APR 2001

PATENT
Docket No. H 3475 PCT/US

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of:
Huber Schenkel

International Application No. PCT/EP99/07143
International Filing Date: September 25, 1999

Serial No. To be assigned **Examiner:** To be assigned
Filed: To be assigned **Art Unit:** To be assigned

Title: IMPACT-RESISTANT EPOXIDE RESIN COMPOSITIONS

"Express Mail Post Office to Addressee" service mailing label Number EL615776154US

PRELIMINARY AMENDMENT

Box PCT
Assistant Commissioner for Patents
Washington, DC 20231

Attn: DO/EO/US

Sir:

Prior to examining this application, please amend the application as follows:

In the Specification (Using the English Translation):

On page 1 of the English translation, on a separate line between the title and line 1, please insert the following:

-- CROSS REFERENCE TO RELATED APPLICATIONS

This application is a national stage application under 35 U.S.C. § 371 of international application PCT/EP99/07143 filed on September 25, 1999, the international

application not being published in English. This application also claims priority under 35 U.S.C. §119 to DE 198 45 607.7 filed on October 6, 1998.

FIELD OF THE INVENTION --.

On page 1, between lines 9 and 10, please insert the header
-- BACKGROUND OF THE INVENTION -- .

On page 5, between lines 22 and 23, please insert the header:
-- DETAILED DESCRIPTION OF THE INVENTION --.

On page 19, line 1, please delete the heading "CLAIMS" and insert therefor:
-- What is claimed is: --

On a separate page, after page 21, please insert the enclosed Abstract of the Disclosure.

In the Claims

Please cancel claims 1 to 14, without prejudice.

Please add the following new claims:

15. (New) A composition comprising

(a) at least one copolymer having at least one glass transition temperature of -30°C or lower and one or more epoxy-reactive groups;

(b) a product bearing one or more terminal phenolic or amino groups wherein the product is formed by a reaction comprising (i) reacting a stoichiometric excess of at least one carboxylic anhydride or carboxylic dianhydride with at least one diamine or polyamine; and (ii) reacting one or more of the excess carboxylic anhydride groups or carboxylic acid groups derived from the excess anhydride groups with a stoichiometric excess of at least one polyphenol or aminophenol; and

(c) at least one first epoxy resin.

16. (New) The composition of claim 15, wherein the copolymer comprises polymerized units of butadiene.

17. (New) The composition of claim 16 wherein the copolymer comprises one or more carboxyl groups and comprises polymerized units of butadiene and acrylonitrile monomer, butadiene and acrylate monomer, butadiene and methacrylate monomer, butadiene, acrylonitrile and styrene monomer, butadiene, acrylate and styrene monomer, or butadiene, methacrylate and styrene monomer.

18. (New) The composition of claim 15 wherein the copolymer is a core/shell polymer comprising:

(i) at least one core polymer comprising a diene polymer, an acrylate polymer, or a methacrylate polymer, wherein the core polymer has a glass transition temperature of -30°C or lower; and

(ii) at least one shell polymer comprising polymerized units of alkyl acrylate, alkyl methacrylate, acrylonitrile, methacrylonitrile, styrene, methylstyrene, olefinically unsaturated carboxylic acids or olefinically unsaturated carboxylic anhydrides or combinations thereof, wherein the shell polymer has a glass transition temperature of 60°C or higher.

19. (New) The composition of claim 18 wherein the core polymer is crosslinked with a diolefinic comonomer.

20. (New) The composition of claim 15 wherein the epoxy reactive groups of the copolymer have been reacted with a second epoxy resin to form an adduct of the second epoxy resin and the copolymer.

21. (New) The composition of claim 15 wherein the carboxylic anhydride or dianhydride of component (b) is selected from the group consisting of maleic anhydride, succinic anhydride, glutaric anhydride, adipic anhydride, pimelic anhydride, suberic anhydride, azelaic anhydride, sebacic anhydride phthalic anhydride, benzenetricarboxylic anhydride, mellophanic dianhydride, pyromellitic dianhydride, 1,8:4,5-naphthalenetetracarboxylic dianhydride, 2,3:6,7-naphthalenetetracarboxylic dianhydride, perylene dianhydride, biphenyl tetracarboxylic dianhydride, diphenylether tetracarboxylic dianhydride, diphenylmethane tetracarboxylic dianhydride, 2,2-diphenylpropane tetracarboxylic dianhydride, benzophenone tetracarboxylic dianhydride and mixtures thereof, and wherein the diamine or polyamine of component (b) is selected from the group consisting of amino-terminated polyethylene glycol, amino-terminated polypropylene glycol, amino-terminated polyoxytetramethylene, amino-terminated polybutadiene and combinations thereof.

22. (New) The composition of claim 21 wherein the product bearing one or more terminal phenolic or amino groups is dissolved in a liquid polyepoxide that is the same as or different from the first epoxy resin.

23. (New) The composition of claim 21 wherein the product bearing one or more terminal phenolic or amino groups is reacted with a stoichiometric excess of a polyepoxide.

24. (New) The composition of claim 21 further comprising at least one latent hardener or accelerator or combinations thereof wherein the hardener or accelerator is selected from the group consisting of guanidines, substituted guanidines, substituted ureas, melamine resins, guanamine derivatives, cyclic tertiary amines, aromatic amines, imidazole derivatives and mixtures thereof.

25. (New) The composition of claim 24 further comprising one or more additives selected from the group consisting of plasticizers, reactive diluents, rheology aids, fillers, wetting agents, antiagers, stabilizers, and combinations thereof.

26. (New) The composition of claim 15 further comprising at least one latent hardener or accelerator or combinations thereof wherein the hardener or accelerator is selected from the group consisting of guanidines, substituted guanidines, substituted ureas, melamine resins, guanamine derivatives, cyclic tertiary amines, aromatic amines, imidazole derivatives and mixtures thereof.

27. (New) The composition of claim 26 wherein the composition is a high-strength high-impact structural adhesive for vehicle construction, aircraft construction or rail vehicle construction.

28. (New) The composition of claim 26 wherein the composition is a potting compound in the electrical or electronics industries or a die-attach adhesive for the production of circuit boards.

29. (New) A process for bonding metallic and/or composite materials comprising:
(a) applying the composition of claim 26 to at least one substrate surface;
(b) joining the substrate surface containing the composition with at least one other surface to form a bond located between the surfaces comprising the composition; and
(c) curing the bond by heating the surfaces to a temperature ranging from 80°C to 210°C.

30. (New) The process of claim 29 wherein the composition is pregelled prior to the curing and the temperature during the curing ranges from 120°C to 180°C.

31. (New) A product produced by a process comprising the steps of:
(a) reacting a stoichiometric excess of at least one carboxylic anhydride or carboxylic dianhydride with at least one diamine or polyamine; and
(b) reacting one or more of the excess carboxylic anhydride groups or carboxylic acid groups derived from the anhydride groups with a stoichiometric excess of at least one polyphenol

or aminophenol to form a product bearing one or more terminal phenolic or amino groups.

32. (New) The product of claim 31 further comprising dissolving the product bearing one or more terminal phenolic or amino groups in a liquid polyepoxide.

33. (New) The product of claim 31 wherein the product bearing one or more terminal phenolic or amino groups is reacted with a stoichiometric excess of a polyepoxide.

34. (New) The product of claim 31 further comprising forming a mixture comprising the product bearing one or more terminal phenolic or amino groups and (i) at least one copolymer having at least one glass transition temperature of -30°C or lower and one or more epoxy-reactive groups, and (ii) at least one epoxy resin.

35. (New) The product of claim 34 wherein the mixture further comprises a latent hardener, or an accelerator, or combinations thereof.

36. (New) The product of claim 31 wherein the stoichiometric excess of the carboxylic anhydride or dianhydride is at least two fold relative to the amino groups of the diamine or polyamine.

37. (New) A process for preparing a composition comprising
(a) reacting a stoichiometric excess of at least one carboxylic anhydride or carboxylic dianhydride with at least one diamine or polyamine; and
(b) reacting one or more of the excess carboxylic anhydride groups or carboxylic acid groups derived from the anhydride groups with a stoichiometric excess of at least one polyphenol or aminophenol to form a product bearing one or more terminal phenolic or amino groups.

38. (New) The process of claim 37 further comprising combining the product bearing one or more terminal phenolic or amino groups with at least one copolymer having at least one glass transition temperature of -30°C or lower and one or more epoxy-reactive groups to form a composition.

39. (New) The process of claim 38 wherein the copolymer, the product bearing one or more terminal phenolic or amino groups, or both are reacted with one or more epoxy resins prior to being combined.

40. (New) The process of claim 39 wherein the composition further comprises at least one second epoxy resin.

41. (New) The process of claim 40 wherein the composition further comprises at least one hardener, accelerator or combinations thereof.

42. (New) The process of claim 41 further comprising heating the composition to a temperature ranging from 80°C to 210°C to harden the composition.

43. (New) The process of claim 37 wherein the stoichiometric excess of carboxylic anhydride or dianhydride is at least two fold relative to the amino groups of the diamine or polyamine.

REMARKS

Applicant respectfully requests the Examiner to enter the above amendments prior to examination of this application.

Status of Claims

Claims 15 to 43 will be pending after entry of the present amendment. Claims 1 to 14 are being canceled without prejudice.

Amendment

The specification is being amended to insert section headers and an abstract of the disclosure in accordance with 37 CFR §1.77 to better conform with US patent practice. The specification is also being amended to insert a cross-reference to related applications in accordance 37 CFR §1.78 and to claim priority to those applications listed therein.

New claims 15 to 43 replace original claims 1 to 14, and are being presented to better conform with US patent practice. These new claims are supported by the specification for example as shown in the Table below (cites to the specification are for the English translation):

Claim	Support in Specification
15, 34, 38, 43	Page 5, lines 23 to 30, page 6, lines 1 to 5, page 7, lines 22 to 28
16 to 19	page 6, line 6 to page 7, line 1
20, 23, 33, 39,40	Page 6, lines 2 to 5
21	Page 8, lines 1 to 21
22, 32	Page 9, lines 24 to 26, page 10, lines 21 to 23
24, 26, 35, 41	Page 11, line 6 to page 12, line 5
25	Page 12, lines 11 to 14
27, 28	page 1, lines 10 to 16, page 13, lines 8 to 16
29, 30	Original claim 14
31, 36, 37	page 7, lines 22 to 28
42	Original claim 11

No new matter is added by the new claims or amendments to the specification.

CONCLUSION

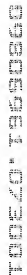
Applicant respectfully requests early and favorable notification of allowance of all pending claims. The Assistant Commissioner is authorized to charge any deficiency in the required fee or to credit any overpayment to Deposit Account 01-1250 in connection with this amendment.

Respectfully submitted,



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Abstract of the Disclosure

The present invention relates to phenol terminated or amino terminated products and compositions containing the same. The phenol-terminated or amino-terminated products are produced by reacting a stoichiometric excess of a carboxylic anhydride or dianhydride with a diamine or polyamine, and reacting the excess carboxylic anhydride groups or carboxylic acid groups with at least one polyphenol or aminophenol to form the phenol-terminated or amino-terminated products. The compositions of the present invention contain (a) a copolymer having at least one glass transition temperature of -30°C or lower and one or more epoxy-reactive groups, (b) the phenol-terminated or amino-terminated product, and (c) at least one epoxy resin. The compositions are preferably used as adhesives.

Impact-resistant Epoxide Resin Compositions

This invention relates to mixtures of special copolymers having at least one glass transition temperature of -30°C or lower and phenol-terminated polyamides or polyimides, mixtures of these components with epoxy resins and/or adducts of epoxy resins with the copolymer having a low glass transition temperature and/or the polyamide or the polyimide and heat-activatable latent hardeners for the resin components and optionally accelerators, fillers, thixotropicizing agents and other typical additives. The invention also relates to a process for the production of these compositions and to their use as a reactive adhesive.

- Reactive epoxy-based hotmelt adhesives are known. In machine and vehicle construction and especially in the construction of aircraft, railway vehicles and motor vehicles, components of various metals and/or composite materials are increasingly being joined together with the aid of adhesives. Epoxy adhesives are widely used for high-strength structural bonding, more particularly as heat-curing one-component adhesives which, in many cases, are also formulated as reactive hotmelts. Reactive hotmelts are adhesives which are solid at room temperature and which soften and behave like a thermoplastic material at temperatures of up to about 80 to 90°C . It is only at relatively high temperatures of about 100°C and higher that the latent hardeners present in these hotmelt adhesives are thermally activated so that irreversible curing to a thermoset occurs. To join the components together, for example in the vehicle industry, the adhesive is first applied warm to at least one substrate surface, after which the parts to be joined are then fitted together. The adhesive then solidifies on cooling and, through this physical solidification, establishes adequate handling resistance, i.e. a temporary bond. The parts thus joined together are further treated in various washing, phosphating and dip painting baths.

It is only after this that the adhesive is cured at relatively high temperatures in an oven.

- Conventional adhesives and hotmelt adhesives based on epoxy resins are hard and brittle in the cured state. Although the bonds obtained with them are generally characterized by very high tensile shear strength, the adhesives flake off under peel, impact or impact/peel stress, particularly at relatively low temperatures, so that loss of bond strength readily occurs when the adhesive joint is subjected to that kind of stress. Accordingly, numerous proposals have already been put forward with a view to so modifying epoxy resins by flexible additives that their brittleness is clearly reduced. One known process is based on the use of special rubber/epoxy resin adducts which are incorporated as heterodisperse phase in the epoxy resin matrix so that the epoxies become more impact-resistant. These epoxy resin compositions are also referred to as "toughened". Another known modification of epoxy resins of the above-mentioned type consists in the reaction of a carboxyl-terminated polybutadiene-co-acrylonitrile copolymer with an epoxy resin. This rubber/epoxy adduct is then dispersed in one or more different epoxy resins. The reaction of the epoxy resin with the carboxyl-containing butadiene/acrylonitrile rubber has to be conducted in such a way that the adduct is not prematurely cured. Although correspondingly modified epoxy resin compositions already represent a clear improvement over unmodified epoxy resins in relation to their impact strength, their behavior under peel or impact/peel stress is still not satisfactory.
- EP-A-0 343 676 describes hotmelt adhesive compositions made up of a mixture of several epoxy resins, a phenolic resin and a polyurethane/epoxy adduct. The polyurethane/epoxy adduct present therein consists of a reaction product of several polyalkylene glycol homopolymers and copolymers containing primary and secondary OH groups, a diisocyanate and at least one epoxy resin. According to the

document in question, these hotmelt adhesive compositions show improved shear resistance, peel strength and impact strength in relation to various commercial one-component hotmelt adhesive compositions. Unfortunately, there is no reference to the adhesive properties of the cured adhesive joint at low temperatures.

US-A-5 290 857 describes an epoxy resin adhesive composition containing an epoxy resin and a powder-form core/shell polymer and a heat-activatable hardener for the epoxy resin. The powder-form core/shell polymer is composed of a core containing an acrylate or methacrylate copolymer with a glass transition temperature of -30°C or lower and a shell containing an acrylate or methacrylate copolymer which contains crosslinking monomer units and which has a glass transition temperature of 70°C or higher, the ratio by weight of the core to the shell being between 10:1 and 1:4. These compositions are said to have excellent adhesive properties, such as peel strength, tensile shear strength and T-peel strength, and also good partial gellability. No mention is made of the properties of bonds with these adhesives at low temperatures.

Similarly, US-A-5,686,509 describes an adhesion-strengthening composition for epoxy resins consisting of powder-form copolymer particles ionically crosslinked with a mono- or divalent metal cation. The core of the core/shell polymer is composed of a diene monomer and optionally crosslinking monomer units and has a glass transition temperature of -30°C or lower. The shell copolymer has a glass transition temperature of at least 70°C and is made up of acrylate or methacrylate monomer units and radically polymerizable unsaturated carboxylic acid units. The adhesive composition is said to contain 15 to 60 parts by weight of the adhesion-strengthening copolymer powder and 3 to 30 parts by weight of a heat-activatable hardening agent to 100 parts of epoxy resin. These compositions are recommended for use as structural adhesives for automobile parts. No mention is made of the low temperature properties of

corresponding bonds.

EP-A-0 308 664 describes epoxy resin compositions which contain an epoxide adduct of a carboxyl-containing copolymer based on butadiene/acrylonitrile or similar butadiene copolymers and a reaction product of an elastomeric isocyanate-terminated prepolymer soluble or dispersible in epoxy resins with a polyphenol or aminophenol and subsequent reaction of this adduct with an epoxy resin. In addition, these compositions may contain one or more epoxy resins. Furthermore, aminofunctional hardeners, polyaminoamides, polyphenols, polycarboxylic acids and their anhydrides or catalytic hardeners and optionally accelerators are proposed for hardening these compositions. The compositions in question are said to be suitable as adhesives which can have high strength, a high glass transition temperature, high peel strength, high impact strength or high tear propagation resistance according to their particular composition.

Similarly, EP-A-0 353 190 describes epoxy resin compositions containing an adduct of an epoxy resin and a carboxylated butadiene/acrylonitrile copolymer and a reaction product of a hydroxyl-, mercapto- or amino-terminated polyalkylene glycol with a phenol carboxylic acid with subsequent reaction of the phenolic group with an epoxy resin. According to EP-A-0 353 190, these compositions are suitable for the production of adhesives, adhesive films, patches, sealing compounds, paints or matrix resins.

According to the teaching of EP-A-0 354 498 or EP-A-0 591 307, reactive hotmelt adhesive compositions can be produced from a resin component, at least one heat-activatable latent hardener for the resin component and optionally accelerators, fillers, thixotropicizing agents and other typical additives, the resin component being obtainable by the reaction of an epoxy resin solid at room temperature and an epoxy resin liquid at room temperature with one or more linear or branched amino-

terminated polyoxypropylenes. The epoxy resins are said to be used in such a quantity, based on the amino-terminated polyoxypropylene, that an excess of epoxy groups, based on the amino groups, is guaranteed. These adhesive compositions have a high peel resistance in the T-peel test which they retain even at low temperatures.

The problem addressed by the present invention was further to improve reactive adhesives of the type mentioned at the beginning to the extent that they would have adequate flexibility and increased peel strength not only at room temperature but also - and in particular - at low temperatures below 0°C. In particular, they would show high peel strength at low temperatures and under sudden stress so that, even in the event of a crash, structurally bonded parts would meet modern safety standards in vehicle construction. These improvements would be obtained without any deterioration in peel strength at high temperatures or in tensile shear strength. In addition, the reactive adhesives would have to exhibit adequate wash-out resistance immediately after application and before final curing. To that end, the adhesive compositions would have to lend themselves as hotmelts to formulation as a highly viscous adhesive suitable for warm application. Another possibility would be to formulate the compositions as an adhesive that could be gelled by a thermal preliminary reaction in a so-called "white body oven" or by induction heating of the joined parts.

The solution provided by the invention to the problem as stated above is defined in the claims and consists essentially in the provision of compositions which contain

- A) a copolymer having at least one glass transition temperature of -30°C or lower and epoxy-reactive groups,
- B) a reaction product of a di- or polyamine with a carboxylic anhydride and a polyphenol or aminophenol and
- C) at least one epoxy resin.

Components A), B) and C) may also be mixtures of compounds of the type mentioned. Components A) and B) are preferably reacted with a large stoichiometric excess of epoxy resins in separate reactions and then optionally mixed with other epoxy resins, heat-activatable hardeners and/or other additives.

Examples of the copolymers of component A) are 1,3-diene polymers containing carboxyl groups and other polar ethylenically unsaturated comonomers. The diene may be butadiene, isoprene or chloroprene and is preferably butadiene. Examples of polar ethylenically unsaturated comonomers are acrylic acid, methacrylic acid, lower alkyl esters of acrylic or methacrylic acid, for example methyl or ethyl esters thereof, amides of acrylic or methacrylic acid, fumaric acid, itaconic acid, maleic acid or lower alkyl esters or semiesters thereof or maleic acid or itaconic anhydride, vinyl esters, such as for example vinyl acetate or - more particularly - acrylonitrile or methacrylonitrile. Most particularly preferred copolymers A) are carboxyl-terminated butadiene/acrylonitrile copolymers (CTBN) which are commercially available in liquid form under the name of Hycar from B.F. Goodrich. These copolymers have molecular weights of 2,000 to 5,000 and acrylonitrile contents of 10% to 30%. Actual examples are Hycar CTBN 1300 X 8, 1300 X 13 or 1300 X 15.

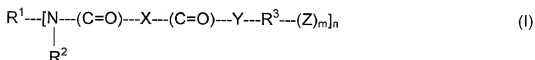
The core/shell polymers known from US-A-5,290,857 and from US-A-5,686,509 may also be used as component A). The core monomers should have a glass transition temperature of or below -30°C and may be selected from the group of diene monomers as mentioned above or suitable acrylate or methacrylate monomers. The core polymer may optionally contain crosslinking monomer units in small quantities. The shell is made up of copolymers which have a glass transition temperature of at least 60°C . The shell is preferably made up of lower alkyl acrylate or methacrylate monomer units (methyl or ethyl esters) and polar monomers, such as (meth)acrylonitrile, (meth)acrylamide, styrene or radical-

polymerizable unsaturated carboxylic acids or carboxylic anhydrides.

However, the adducts of epoxy resins and the liquid CTBN rubbers mentioned above are particularly preferred for component A).

Component B) may be represented by the following formula I:

5



10 in which

m = 1 or 2,

n = 2 or 3,

R¹ is an amino-terminated residue of a polyalkylene glycol after removal of the functional groups,

15 R² = H, C₁₋₆ alkyl, aryl or -(C=O)-; where R² = -(C=O)-, the two carbonyl groups, the nitrogen and X form a five-membered cyclic imide ring,

X = C₂₋₆ alkyl or the residue of an aromatic carboxylic anhydride or dianhydride after removal of the cyclic anhydride group(s),

Y = -O-, -S- or -NR⁴-, where R⁴ = H or C₁₋₄ alkyl or phenyl,

20 R³ is a carbocyclic-aromatic or araliphatic m+1-functional residue with groups Z directly attached to the aromatic ring and Z = O, H or -NHR⁴.

Component B) is a reaction product of a di- or polyamine and a carboxylic anhydride, the stoichiometric ratio being selected so that the carboxylic anhydride is preferably in a two-fold excess over the amino
25 groups, after which the remaining carboxylic anhydride groups or carboxylic acid groups are reacted with a polyphenol or aminophenol in a stoichiometric excess so that the condensation product bears terminal phenolic or amino groups. This condensation product is generally mixed directly into the compositions according to the invention although it may
30 also be reacted with a large stoichiometric excess of epoxy resins so that an epoxy-terminated condensation product is formed.

In principle, a large number of diamines or polyamines may be used for the condensation although amino-terminated polyalkylene glycols, more particularly di- or trifunctional amino-terminated polypropylene glycols, polyethylene glycols or copolymers of propylene glycol and ethylene glycol, are preferably used. These glycols are also known under the name of "Jeffamine" (Huntsman). The amino-terminated polyoxytetramethylene glycols, also known as Poly-THF, are also particularly suitable. Other suitable synthesis components are amino-terminated polybutadienes. The amino-terminated polyalkylene glycols have molecular weights of 400 to 5,000.

Examples of suitable carboxylic anhydrides are maleic, succinic, glutaric, adipic, pimelic, suberic, azelaic or sebacic anhydride or, more particularly, anhydrides or dianhydrides of aromatic carboxylic acids or hydrogenation products thereof, such as phthalic anhydride, benzenetricarboxylic anhydride, tetrahydrophthalic dianhydride, mellophanic dianhydride, pyromellitic dianhydride, 1,8:4,5- and 2,3:6,7-naphthalenetetracarboxylic dianhydride, perylene dianhydride, biphenyl tetracarboxylic acid dianhydride, diphenylether tetracarboxylic dianhydride, diphenylmethane tetracarboxylic dianhydride, 2,2-diphenylpropane tetracarboxylic dianhydride or benzophenone tetracarboxylic dianhydride and mixtures thereof.

Besides the carboxylic anhydrides mentioned above, maleinized oils and fats may also be used as anhydride components for the preparation of condensation product B). Maleinized oils and fats and low molecular weight polyenes are known to be prepared by ene reaction or by free radical reaction of maleic anhydride with unsaturated compounds.

The polyphenols or aminophenols to be used for condensation product B) are either aromatic di- or trihydroxy compounds derived from a mono- or polynuclear carbocyclic-aromatic radical or the corresponding aminohydroxy compounds. The aromatic rings may either be condensed

or attached to one another by binding links or by a covalent bond.

Examples of the compounds mentioned first are hydroquinone, resorcinol, pyrocatechol, isomers of dihydroxynaphthalene (pure isomers or mixture of several isomers), isomers of dihydroxyanthracene and the corresponding aminohydroxy compounds. The polyphenols or aminophenols, which are derived from carbocyclic-aromatic compounds of which the aromatic nuclei are attached by binding links, may be represented by the following general formula II:



in which Z is as defined above,

AR is a mononuclear aromatic radical which may optionally be further substituted by alkyl or alkenyl radicals,

- 15 B stands for the binding link which may be selected from the group consisting of a covalent bond, $-CR^5R^6-$, $-O-$, $-S-$, $-SO_2-$, $-CO-$, $-COO-$, $-CONR^7-$ and SiR^8R^9- where R^5 , R^6 and R^7 independently of one another represent hydrogen, $-CF_3$ or C_{1-6} alkyl or R^5 and R^6 together with the common C atom form a cycloaliphatic radical with 5 to 7 ring C atoms, R^8 and R^9 represent C_{1-6} alkyl. The two groups B and Z in formula II independently of one another may be located in the ortho, meta or para position. Particularly preferred compounds corresponding to formula II are 4,4'-dihydroxydiphenyl or the bisphenols A and/or F.

- 25 Suitable epoxy resins for component C) or for forming the epoxy adduct or for mixing components A) and B) are any of a number of polyepoxides which contain at least two 1,2-epoxy groups per molecule. The epoxy equivalent of these polyepoxides may be between 150 and 4,000. Basically, the polyepoxides may be saturated, unsaturated, cyclic or acyclic, aliphatic, alicyclic, aromatic or heterocyclic polyepoxide compounds. Examples of suitable polyepoxides include the polyglycidyl
- 30

ethers which are obtained by reaction of epichlorohydrin or epibromohydrin with a polyphenol in the presence of alkali. Polyphenols suitable for this purpose are, for example, resorcinol, pyrocatechol, hydroquinone, bisphenol A (bis-(4-hydroxyphenyl)-2,2-propane)), bisphenol F (bis(4-hydroxyphenyl)methane), bis-(4-hydroxyphenyl)1,1-isobutane, 4,4'-dihydroxybenzophenone, bis-(4-hydroxyphenyl)-1,1-ethane, 1,5-hydroxy-naphthalene.

Other polyepoxides suitable in principle are the polyglycidyl ethers of polyalcohols or diamines. These polyglycidyl ethers are derived from polyalcohols, such as ethylene glycol, diethylene glycol, triethylene glycol, 1,2-propylene glycol, 1,4-butylene glycol, triethylene glycol, pentane-1,5-diol, hexane-1,6-diol or trimethylol propane.

Other polyepoxides are polyglycidyl esters of polycarboxylic acids, for example reaction products of glycidol or epichlorohydrin with aliphatic or aromatic polycarboxylic acids, such as oxalic acid, succinic acid, glutaric acid, terephthalic acid or dimer fatty acid.

Other epoxides are derived from the epoxidation products of olefinically unsaturated cycloaliphatic compounds or from native oils and fats.

The epoxy resins obtained by reaction of bisphenol A or bisphenol F are most particularly preferred. Mixtures of liquid and solid epoxy resins are generally used, the liquid epoxy resins preferably being based on bisphenol A and having a sufficiently low molecular weight. Epoxy resins liquid at room temperature which generally have an epoxy equivalent weight of 150 to about 220 and more particularly in the range from 182 to 192 are particularly preferred for the adduct formation of components A) and B).

The hardness of the reactive adhesive in the cooled state, i.e. in particular after application to the substrate to be joined, but before curing, depends on the degree of condensation and hence molecular weight of

component B) in particular and on the ratio of solid epoxy resin to liquid epoxy resin. The higher the degree of condensation (and hence the molecular weight) of condensation product B) and the greater the proportion of solid epoxy resin in the composition, the harder the cooled semicrystalline adhesive will be.

Suitable heat-activatable or latent hardeners for the epoxy resin binder system of components A), B) and C) are guanidines, substituted guanidines, substituted ureas, melamine resins, guanamine derivatives, cyclic tertiary amines, aromatic amines and/or mixtures thereof. The hardeners may be stoichiometrically included in the curing reaction although they may also be catalytically active. Examples of substituted guanidines are methyl guanidine, dimethyl guanidine, trimethyl guanidine, tetramethyl guanidine, methyl isobiguanidine, dimethyl isobiguanidine, tetramethyl isobiguanidine, hexamethyl isobiguanidine, heptamethyl isobiguanidine and, most particularly, cyanoguanidine (dicyanodiamide). Alkylated benzoguanamine resins, benzoguanamine resins or methoxymethyl ethoxymethyl benzoguanamine are mentioned as representatives of suitable guanamine derivatives. The selection criterion for the one-component heat-curing hotmelt adhesives is of course their low solubility at room temperature in the resin system so that solid finely ground hardeners are preferred, dicyanodiamide being particularly suitable. The composition is thus guaranteed a long shelf life.

Catalytically active substituted ureas may be used in addition to or instead of the hardeners mentioned above. These substituted ureas are, in particular, p-chlorophenyl-N,N-dimethyl urea (Monuron), 3-phenyl-1,1-dimethyl urea (Fenuron) or 3,4-dichlorophenyl-N,N-dimethyl urea (Diuron). In principle, catalytically active tertiary aryl or alkyl amines, for example benzyl dimethyl amine, tris(dimethylamino)phenol, piperidine or piperidine derivatives, may also be used, but often have too high a solubility in the adhesive system so that the one-component system is not guaranteed

useful shelf life in their case. In addition, various, preferably solid imidazole derivatives may be used as catalytically active accelerators. 2-Ethyl-2-methyl imidazole, N-butyl imidazole, benzimidazole and N-C₁₋₁₂-alkyl imidazoles or N-arylimidazoles are mentioned as representatives of such
5 accelerators.

In addition, the adhesives according to the invention contain fillers known per se such as, for example, the various ground or precipitated chalks, carbon black, calcium-magnesium carbonates, heavy spar and, in particular, silicate fillers of the aluminium-magnesium-calcium silicate type,
10 for example wollastonite, chlorite.

The adhesive compositions according to the invention may also contain other typical auxiliaries and additives such as, for example, plasticizers, reactive diluents, rheology aids, wetting agents, antiagers, stabilizers and/or pigments.

The adhesives according to the invention may be formulated on the one hand as one-component adhesives which in turn may be formulated both as highly viscous adhesives designed for warm application and as heat-activatable hotmelt adhesives. These adhesives may also be formulated as one-component pregellable adhesives, in which case the
15 compositions contain either fine-particle thermoplastic powders such as, for example, polymethacrylates, polyvinyl butyral or other thermoplastic (co)polymers or the curing system is so adapted that a two-stage curing process occurs, the gelling step effecting only partial curing of the adhesive and final curing in vehicle construction taking place, for example, in one of
20 the paint ovens, preferably the cathodic electrodeposition oven.

The adhesive compositions according to the invention may also be formulated as two-component epoxy adhesives where the two reaction components are only mixed just before application, curing then taking place at room temperature or moderately elevated temperature. The second
25 reaction component may be selected from the reaction components known

per se for two-component epoxy adhesives, for example di- or polyamines, amino-terminated polyalkylene glycols (for example Jeffamine, Amino-Poly-THF) or polyaminoamides. Other reactants may be mercaptofunctional prepolymers such as, for example, the liquid Thiokol polymers. Basically, the epoxy compositions according to the invention may also be cured with carboxylic anhydrides as the second reaction component in two-component adhesive formulations.

Besides the applications mentioned at the beginning, the adhesive compositions according to the invention may also be used as potting compounds in the electrical or electronics industries and as die-attach adhesives in electronics for bonding components to circuit boards. Other possible applications for the compositions according to the invention are as matrix materials for composite materials such as, for example, fiber-reinforced composites.

However, a most particularly preferred application for the adhesives according to the invention is structural bonding in vehicle construction.

The quantity ratios between the individual components may vary within relatively wide limits, depending on the requirements the adhesive is expected to satisfy in regard to its application properties, flexibility, impact peel strength or tensile strength. Typical ranges for the key components are:

- component A) 5-25% by weight, preferably 1-20% by weight
- component B): 5-30% by weight, preferably 5-20% by weight
- component C): 10-45% by weight, preferably 15-30% by weight; this component may be composed of one or more liquid and/or solid epoxy resins in which case it may optionally contain low molecular weight epoxides as reactive diluents
- fillers: 10-40% by weight
- hardener component (for heat-curable one-component systems): 1-10% by weight, preferably 3-8% by weight

- accelerator: 0.01-3% by weight, preferably 0.1 to 0.8% by weight
- rheology aid (thixotropicizing agent): 0.5-5% by weight.

As mentioned at the beginning, the requirements modern structural adhesives are expected to meet in vehicle construction continue to increase because more and more structural elements - including those with load-bearing functions - are being joined by bonding processes. As already stated in the article by G. Lötting and S. Singh entitled: "Anforderungen an Klebstoffe für Strukturverbindungen im Karosseriebau" Adhesion 1988, No. 9, pages 19 to 26, the adhesives are expected on the one hand to fulfil production aspects of practical relevance, including automatable application in short cycle times, adhesion to oil-covered metal panels, adhesion to various types of metal panels and compatibility with the process conditions on the paint line (resistance to washing and phosphating baths, curability during stoving of the CED primer, resistance to the following painting and drying operations). In addition, modern structural adhesives have to exhibit improving strength and deformation properties, even in the cured state. These include the high corrosion resistance and flexural strength of the structural components and the deformability of the bond under mechanical stress. High deformability of the structural components guarantees a considerable safety advantage in the event of a crash. This crash behavior can best be determined by determining the impact energy for cured bonds; sufficiently high values for impact energy or impact/peel energy are desirable both at high temperatures of up to +90°C and in particular at low temperatures down to -40°C. High tensile shear strength should also be achieved. Both strengths should be achieved on a large number of substrates, mainly oil-covered metal panels, for example steel bodywork panels, steel plate galvanized by various methods, panels of various aluminium alloys or even magnesium alloys and steel plates coated by coil coating with organic coatings of the "Bonazinc" or "Granocoat" type. As shown in the following

Examples, the adhesive compositions according to the invention surprisingly satisfy these requirements to a very high degree.

The following Examples are intended to illustrate the invention. All quantities in connection with the compositions are parts by weight, unless
5 otherwise indicated.

General procedure for producing component A)

A carboxy-terminated poly(butadiene-co-acrylonitrile) (Hycar CTBN 1300 X 13) was reacted for 3 hours with stirring under nitrogen at 140°C
10 with an approximately 10-molar excess of a liquid DGEBA epoxy resin until the reaction was constant.

General procedure for preparing condensation product B)

In a stirrable and heatable tank reactor, 1 mole of the carboxylic
15 anhydride or dicarboxylic anhydride were reacted under nitrogen for 3 to 4 hours at 120°C to 160°C with 0.4 to 0.7 mole of an amino-terminated polyalkylene glycol, the polyamine being introduced into the reactor first and heated initially to 130°C. The adduct thus formed was reacted with
about 1.1 to 1.5 moles of a polyphenol until the reaction was constant. The
20 progress of the reaction was followed by gel permeation chromatography (GPC). This phenol-terminated polymer was then mixed with an epoxy resin, preferably a diglycidyl ether of bisphenol A (DGBEA).

General production of the adhesive

25 In a kneader, components A), B) and a liquid epoxy resin and a solid epoxy resin were mixed to homogeneity at room temperature or optionally at 80°C in the presence of the fillers, hardeners, accelerators and rheology aids and the resulting mixture was poured into the storage containers optionally while still warm.

Examples 1 to 6

The condensation products B) listed in Table 1 were prepared from Jeffamine-D-2000 (polyoxypropylenediamine, molecular weight 2000), pyromellitic dianhydride and resorcinol by the general method for preparing the condensation product B).

Table 1.

Example	1	2	3	4	5	6
D-2000	219.0	229.5	222.0	235.5	237.6	200.0
PMSA	48.0	42.0	48.0	41.4	36.9	31.3
Resorcinol	33.0	28.5	30.0	31.2	25.5	18.7

D-2000 = Jeffamine D-2000

PMSA = pyromellitic dianhydride

Component A) was prepared from Hycar CTBN 1300 X13 and a liquid DGBEA resin by the method described above. The resulting composition contained 40% butyl rubber and had an epoxy equivalent weight of 900 and a viscosity at 80°C of 200 Pa.s.

Examples 7 to 12

Adhesive compositions according to the invention were prepared from components B) of to Examples 1 to 6, component A) and a liquid DGEBA resin (epoxy equivalent weight 189), fillers, dicyanodiamide as hardener and accelerators and hydrophobic silica as thixotropizing agent. The compositions are set out in Table 2.

Table 2. Adhesives according to the invention

Example	7	8	9	10	11	12
Component B) of Example 1	13.5					
Component B) of Example 2		13.5				
Component B) of Example 3			13.5			
Component B) of Example 4				13.5		
Component B) of Example 5					13.5	
Component B) of Example 6						13.5
Component A)	17.0	17.0	17.0	17.0	17.0	17.0
DGEBA resin, liquid	28.0	28.0	28.0	28.0	28.0	28.0
Wollastonite	33.7	33.7	33.7	33.7	33.7	33.7
Dicyanodiamide	4.5	4.5	4.5	4.5	4.5	4.5
Fenuron	0.3	0.3	0.3	0.3	0.3	0.3
Silica, hydrophobic	3.0	3.0	3.0	3.0	3.0	3.0

Wollastonite filler

Silica: Carbosil TS 720

The adhesive properties of the Examples according to the invention and the adhesive properties of known adhesives are compared in Table 3. The adhesive of Comparison Example 1 was Terokal 5051 of Henkel Teroson which had been made in accordance with the teaching of EP-A-0 354 498. The adhesive of Comparison Example 2 was Betamate 1044/3 made by Gurit Essex. It is assumed that this adhesive had been produced in accordance with the teaching of EP-A-0 308 664

Table 3. Adhesive properties

Example	7	8	9	10	11	12	Comp. 1	Comp. 2
Impact -40°C [J]	8.7	11.7	9.4	13.1	6.7	0.7	0.5	3.3
Impact -20°C [J]	12.7	14.7	13.4	16.2	10.5	1.9	0.4	2.6
Impact 0°C [J]	13.2	13.6	15.0	16.8	12.1	3.9	0.9	4.4
Impact RT [J]	15.5	14.7	16.1	16.0	12.9	5.0	2.1	5.2
TSS -40°C [Mpa]	34.1 scf	31.1 scf	25.2 scf	30.9 cf	28.4 cf	37.8; 80% cf	19.8 cf	20.2 cf
TSS RT [Mpa]	25.7 cf	22.7 cf	21.6 cf	22.5 cf	18.7 cf	16.4; 80% cf	21.8 cf	21.6 cf
TSS +90°C [Mpa]	14.8 c	11.9 cf	11.4 cf	12.0 cf	11.0 cf	12.4 cf	10.9 cf	11.1 cf
500 h SST	20.3 c	17.0 cf	17.0 cf	18.9 cf	17.0 cf	n.a.	19.3 cf	18.8 cf
1000 h SST	19.1 c	17.9 cf	14.5 cf	18.2 cf	16.6 cf	n.a.	17.5 cf	16.7 cf

Impact: impact peel test to ISO 11343 at 2 m/sec

RT: room temperature

TSS: tensile shear strength to DIN 53283

TSS: salt spray test to DIN 50021

cf: cohesive fracture pattern 100% unless otherwise indicated

scf: cohesive fracture pattern with partial film residue on a substrate

As these test results show, the impact peel energy to ISO 11343 of the adhesives according to the invention is several times higher than that of the known adhesives. At very low temperatures in particular, the impact peel energy of the adhesives according to the invention is clearly better than that of the known adhesives without any deterioration in tensile shear strength or ageing behavior in the salt spray test.

CLAIMS

1. A composition obtainable by reacting a carboxylic anhydride or carboxylic dianhydride with a diamine or polyamine and a polyphenol or aminophenol.

5 2. A composition containing

A) a copolymer having at least one glass transition temperature of -30°C or lower and epoxy-reactive groups,

B) a reaction product obtainable by reacting a carboxylic anhydride or dianhydride with a diamine or polyamine and a polyphenol or aminophenol and

10

C) at least one epoxy resin.

3. Compositions as claimed in claim 2, characterized in that component A) is a butadiene-based copolymer.

4. Compositions as claimed in claim 2 or 3, characterized in that
15 component A) is a carboxyl-containing copolymer based on butadiene/acrylonitrile, butadiene/(meth)acrylates, a butadiene/acrylonitrile/styrene copolymer or a butadiene/(meth)acrylate/styrene copolymer.

5. A composition as claimed in claim 2, characterized in that component A) is a core/shell polymer of which the core polymer is a diene
20 polymer or a (meth)acrylate polymer with a glass transition temperature of -30°C or lower and which may optionally be crosslinked with 0.01 to 5% by weight of a diolefinic comonomer and of which the shell polymer has a glass transition temperature of 60°C or higher and is obtained from monomers from the group consisting of alkyl (meth)acrylate,
25 (meth)acrylonitrile, (methyl) styrene and olefinically unsaturated carboxylic acids or carboxylic anhydrides or mixtures thereof.

6. A composition as claimed in at least one of the preceding claims, characterized in that an adduct of an epoxy resin and a copolymer according to claims 2 to 5 is used as component A).

30 7. A composition as claimed in at least one of the preceding claims,

characterized in that component b) is prepared by condensation from

- a) a carboxylic anhydride selected from maleic, succinic, glutaric, adipic, pimelic, suberic, azelaic or sebacic anhydride or phthalic anhydride, benzenetricarboxylic anhydride, mellophanic dianhydride, pyromellitic dianhydride, 1,8:4,5- and 2,3:6,7-naphthalenetetracarboxylic dianhydride, perylene dianhydride, biphenyl tetracarboxylic dianhydride, diphenylether tetracarboxylic dianhydride, diphenylmethane tetracarboxylic dianhydride, 2,2-diphenylpropane tetracarboxylic dianhydride or benzophenone tetracarboxylic dianhydride and mixtures thereof and
 - b) a polyamine selected from polyethylene glycol, polypropylene glycol, polyoxytetramethylene or polybutadiene diamine or triamine and
 - c) a polyphenol or aminophenol.
8. A composition as claimed in claims 2 to 7, characterized in that component B) according to claim 7 is dissolved in a liquid polyepoxide.
9. A composition as claimed in claims 1 to 5, characterized in that component B) according to claim 7 is reacted with a stoichiometric excess of a polyepoxide.
10. A composition as claimed in at least one of the preceding claims, characterized in that, in addition to components A), B) and C), it contains
- A) a latent hardener from the group consisting of dicyanodiamide, guanamines, guanidines, aminoguanidines, solid aromatic diamines and/or a hardening accelerator and
 - B) optionally plasticizers, reactive diluents, rheology aids, fillers, wetting agents and/or antiagers and/or stabilizers.
11. A process for hardening components A), B), C), D) and optionally E) according to claim 10 by heating the composition to temperatures of 80°C to 210°C and preferably to temperatures of 120°C to 180°C.
12. The use of the compositions claimed in claim 10 as a high-strength high-impact structural adhesive in vehicle construction, aircraft construction

or rail vehicle construction.

13. The use of the compositions claimed in claim 10 for the production of composite materials, as potting compounds in the electrical and electronics industries and as a die-attach adhesive in the production of

5 circuit boards in the electronics industry.

14. A process for bonding metallic and/or composite materials comprising the following key process steps:

- applying the adhesive composition claimed in claim 10 to at least one of the substrate surfaces to be joined, optionally after cleaning and/or surface treatment
- 10 • fitting together the parts to be joined
- optionally pregelling the adhesive composition and
- curing the bond by heating the parts to temperatures of 80°C to 210°C and preferably to temperatures of 120°C to 180°C.

Type a plus sign (+) inside this box ☐

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DECLARATION FOR UTILITY OR DESIGN PATENT APPLICATION

☐ Declaration Submitted with Initial Filing OR ☒ Declaration Submitted after Initial Filing

Attorney Docket
Number
First Named
Inventor

H 3475 PCT/US

Schenkel, Hubert

COMPLETE IF KNOWN

Application Number 09/806,961

Filing Date

Group Art Unit

Examiner Name

As a below named inventor, I hereby declare that

My residence, post office address, and citizenship are as stated below next to my name

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled:

IMPACT-RESISTANT EPOXIDE RESIN COMPOSITIONS

(Title of the Invention)

the specification of which

☐ is attached hereto

OR

☒ was filed on (MM/DD/YYYY)

09/25/1999

as United States Application Number or PCT International

Application Number

PCT/EP99/07143

and was amended on (MM/DD/YYYY)

(if applicable).

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment specifically referred to above.

I acknowledge the duty to disclose information which is material to patentability as defined in Title 37 Code of Federal Regulations, § 1.56.

I hereby claim foreign priority benefits under Title 35, United States Code §119(a)-(d) or §365(b) of any foreign application(s) for patent or inventor's certificate, or §365(e) of any PCT International application which designated at least one country other than the United States of America, listed below and have also identified below, by checking the box, any foreign application for patent or inventor's certificate, or of any PCT International application having a filing date before that of the application on which priority is claimed.

Prior Foreign Application Number(s)	Country	Foreign Filing Date (MM/DD/YYYY)	Priority Not Claimed	Certified Copy Attached?	
198 45 607.7	Germany	10/06/1998	<input type="checkbox"/>	YES <input type="checkbox"/>	NO <input checked="" type="checkbox"/>
			<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
			<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
			<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
			<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>
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I hereby claim the benefit under Title 35, United States Code §119(e) of any United States provisional application(s) listed below

Application Number(s)	Filing Date (MM/DD/YYYY)	Additional provisional application numbers are listed on a supplemental priority sheet attached hereto

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DECLARATION**Page 2**

I hereby claim the benefit under Title 35, United States Code §120 of any United States application(s), or §3650 of any PCT international application designating the United States of America, listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States or PCT international application in the manner provided by the first paragraph of Title 35, United States Code §112 I acknowledge the duty to disclose information which is material to patentability as defined in Title 37, Code of Federal Regulations §1.56 which became available between the filing date of the prior application and the national or PCT international filing date of this application.

U.S. Parent Application Number	PCT Parent Number	Parent Filing Date (MM/DD/YYYY)	Parent Patent Number (if applicable)
	PCT/EP99/07143	09/25/1999	

☐ Additional U.S. or PCT international application numbers are listed on a supplemental priority sheet attached hereto

As a named inventor, I hereby appoint the following attorney(s) and/or agent(s) to prosecute this application and to transact all business in the Patent and Trademark Office connected therewith:

☐ Firm Name Customer Number or label

OR

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Name of Sole or First Inventor:

☐ A petition has been filed for this unsigned inventor

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